

**OPEN ACCESS**

# Positron annihilation lifetime study of interfaces in ternary polymer blends

To cite this article: D Meghala *et al* 2013 *J. Phys.: Conf. Ser.* **443** 012047

View the [article online](#) for updates and enhancements.

**Related content**

- [Interface profile studies in immiscible and partially miscible binary polymer blends from free volume measurement](#)  
P Ramya, D Meghala, T Pasang *et al.*
- [Positron lifetime study of poly\(dimethylsiloxane\) based polymer-nanoparticle composites](#)  
D J Hughes, M V Roussanova, P Beavis *et al.*
- [A free volume approach to the mechanical behaviour of miscible polycarbonate blends](#)  
A J Hill, M D Zipper, M R Tant *et al.*

**IOP | ebooks™**

Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.

Start exploring the collection - download the first chapter of every title for free.

# Positron annihilation lifetime study of interfaces in ternary polymer blends

D Meghala<sup>1, §</sup>, P Ramya<sup>1</sup>, T Pasang<sup>1</sup>, J M Raj<sup>1</sup>, C Ranganathaiah<sup>1,2</sup> and J F Williams<sup>2</sup>

<sup>1</sup>Department of Studies in Physics, University of Mysore, Manasagangotri, Mysore-570 006, India.

<sup>2</sup>ARC Centre of Excellence, Centre for Antimatter-Matter Studies, School of Physics, University of Western Australia, WA 6009, Australia.

**Abstract:** A new method based on positron lifetime spectroscopy is developed to characterize individual interfaces in ternary polymer blends and hence determine the composition dependent miscibility level. The method owes its origin to the Kirkwood-Risemann-Zimm (KRZ) model for the evaluation of the hydrodynamic interaction parameters ( $\alpha_{ij}$ ) which was used successfully for a binary blend with a single interface. The model was revised for the present work for ternary polymer blends to account for three interfaces. The efficacy of this method is shown for two ternary blends namely poly(styrene-*co*-acrylonitrile)/poly (ethylene-*co*-vinylacetate)/poly(vinyl chloride) (SAN/EVA/PVC) and polycaprolactone /poly(styrene-*co*-acrylonitrile)/poly(vinyl chloride) (PCL/SAN/PVC) at different compositions. An effective hydrodynamic interaction parameter,  $\alpha_{eff}$ , was introduced to predict the overall miscibility of ternary blends.

## 1. Introduction

The concept used in the development of ternary polymer blends is that a polymer A, which is miscible with two polymers B and C, can make compatible the immiscible binary pair B and C. Miscibility is governed by the interfacial behavior [1] and, generally, the interface is the region formed between two phases. The interface plays an important role with regard to several properties of the blends so formed and is expected to change with composition.

Studies on ternary polymer blends have reported only the overall nature of the blend and in some cases individual binary blends had been constructed and characterized to understand the influence of individual interfaces in ternary blends [2]. However, this information is indirect and the situation concerning three interfaces in a real ternary blend is different and more complicated compared to single individual interface that exists in a binary blend. To understand better the nature of interfaces at the microscopic level we used the novel approach proposed by Schnell and Wolf [3] for polymer/solvent systems in terms of the hydrodynamic interaction parameter ( $\alpha$ ) evaluated from viscosity measurements. This method was modified by Ranganathaiah et al [4] for polymer/polymer binary blends in the solid phase for the characterization of a single interface by invoking the concept that free volume and viscosity are inversely related [5]. The efficacy of this method has been verified for several binary blend systems under varying conditions [6,7] by the determining hydrodynamic interaction parameter from the measured free volume data obtained from positron lifetime spectroscopy. However, the same approach is not directly applicable to ternary blends with three interfaces. So, for three distinct interfaces, three hydrodynamic interaction parameters are to be formulated one for each interface. Hence, in this work, we have investigated two ternary blend systems namely (1) poly(styrene-*co*-acrylonitrile)/poly (ethylene-*co*-vinylacetate)/poly(vinyl chloride) (SAN/EVA/PVC) and (2) polycaprolactone /poly(styrene-*co*-acrylonitrile)/poly(vinyl

<sup>§</sup> email: meghala.dinesh@gmail.com



chloride) (PCL/SAN/PVC) for different compositions. The required mathematical formulations for three  $\alpha$ 's ( $\alpha_{12}$ ,  $\alpha_{23}$  and  $\alpha_{31}$ ), one for each interface, have been derived and tested experimentally. From our method the individual  $\alpha$ 's are derived and used to compute an effective  $\alpha$  ( $\alpha_{\text{eff}}$ ) using simple additivity rule. The  $\alpha_{\text{eff}}$  facilitate comparison of the present results with published results.

## 2. Experimental

We have prepared the samples of SAN/EVA/PVC and PCL/SAN/PVC ( $T_g$ : SAN:106°C, EVA:-20°C PVC:74°C, PCL:-60°C) of different compositions by the conventional solution casting method using a common solvent tetrahydrofuran (THF). To record lifetime spectra of the blends and the respective individual polymers positron annihilation lifetime spectrometer (PALS) with a time resolution of 220 has been used. A 17  $\mu\text{Ci}$   $^{22}\text{Na}$  positron source on kapton foil backing was used in the measurement of spectra. All the measurements have been done at room temperature in air. The lifetime spectra have been resolved into three lifetime components using computer program PATFIT-88 with proper source and background corrections. Further details can be found from earlier works [6]. The *o*-Ps lifetime  $\tau_3$  and intensity  $I_3$  are used to obtain the fractional free volume  $F_V$  of the blends as well as individual polymers.

## 3. Results & Discussion

Wolf et al [3] introduced two parameters measured from viscosity data; one is the geometric factor ( $\gamma$ ) related to the molecular arrangement and to the architecture of the blend, and the other is the hydrodynamic interaction parameter ( $\alpha$ ) considered as a measure of the excess friction generated at the interface between the blend constituents. The hydrodynamic interaction has its genesis in the KRZ model proposed by Zimm [8] which is an extension of the KSR (Kargin-Slonimsky-Rouse) model proposed by Rouse [9]. According to the KRZ model, 'hydrodynamic interaction' between the polymer and solvent excludes specific interactions but is associated with flow dynamics which influences the visco-elastic behavior of the system either in liquid or solid phase. Further, the friction associated with the visco-elastic flow results in energy dissipation at the interface and is influenced by the composition of the blend. In the case of miscible blends, the polymer chains are brought closer to each other and increase the friction at the interface. Energy dissipation increases and tension at the interface decreases.

The negative sign of the hydrodynamic interaction parameter ( $\alpha$ ) indicates dissipation of energy. If miscibility is high at certain composition of the blend,  $\alpha$  takes large negative values [6]. On the other hand, for immiscible blends,  $\alpha$  is close to zero or positive. This is interpreted as the absence of any favorable interaction between the constituent polymers and hence friction at the interface is very less.

For a ternary polymer blend characterized by three interfaces, we define  $\phi_1$ ,  $\phi_2$ ,  $\phi_3$  as the volume fractions of component polymers 1, 2 and 3 of the blend and  $\alpha_{12}$ ,  $\alpha_{23}$ ,  $\alpha_{31}$  as the hydrodynamic interaction parameters corresponding to interfaces between polymer 1-2, 2-3 and 3-1 respectively, and their relationships as follows.

$$\frac{1}{\Delta F_V} = \delta_1 [\phi_1 - \Omega_1(1 + \Omega_1\Omega_2)] + \delta_2 [\Omega_3(1 - \Omega_2^2) - \phi_3] - \delta_3 \Omega_3^2 \Omega_1 + \sum_{\substack{i,j=1 \\ j=i+1}}^3 \left[ \frac{e^{1/F_{VB}} \rho \Omega_i^2 \Omega_j}{1 + \gamma_{ij}} + 2\alpha_{ij}(1 - \Omega_i)\Omega_i\Omega_j \right] \quad (1)$$

and

$$\frac{1}{\Delta F_V} = \frac{1}{F_{VB}} - \frac{\phi_1}{F_{V1}} - \frac{\phi_2}{F_{V2}} - \frac{\phi_3}{F_{V3}} \quad (2)$$

Here,  $F_{VB}$ ,  $F_{V1}$ ,  $F_{V2}$ ,  $F_{V3}$  are the experimentally measured fractional free volumes of the ternary blend, pure polymers (blend constituents) 1, 2 and 3 respectively,  $\phi_1$ ,  $\phi_2$  and  $\phi_3$  are the volume fractions of the blend components 1, 2 and 3 respectively. Also  $\rho$  is density of the blend and  $\Omega_1$ ,  $\Omega_2$ ,  $\Omega_3$  are the surface fractions given by,

$$\Omega_1 = \frac{(1+\gamma_{12})(1+\gamma_{31})\phi_1}{(1+\gamma_{12})(1+\gamma_{31})\phi_1 + (1+\gamma_{31})\phi_2 + (1+\gamma_{12})\phi_3} \quad \Omega_2 = \frac{(1+\gamma_{23})\phi_2}{(1+\gamma_{12})\phi_1 + (1+\gamma_{23})\phi_2 + \phi_3} \quad \Omega_3 = \frac{\phi_3}{(1+\gamma_{31})\phi_1 + (1+\gamma_{23})\phi_2 + \phi_3} \quad (3)$$

and

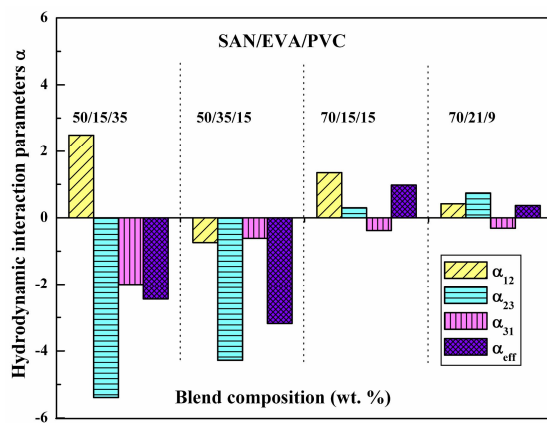
$$\sum_{\substack{i,j=1, \\ j=i+1}}^3 \delta_{ij} = \frac{1}{F_{Vj}} - \frac{1}{F_{Vi}} \quad (4)$$

$\gamma$  is the geometric factor given by

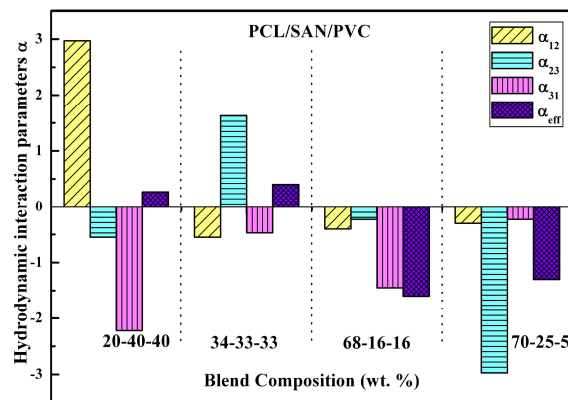
$$\frac{1}{F_{VB}} = \frac{\phi_1}{F_{V1}} + \frac{\phi_2}{F_{V2}} + \frac{\phi_3}{F_{V3}} + \sum_{\substack{i,j=1 \\ j=i+1}}^3 \left[ \left( \frac{1}{F_{Vj}} - \frac{1}{F_{Vi}} \right) \left( \frac{\gamma_{ij} \phi_j \phi_i}{1 + \gamma_{ij} \phi_j} \right) \right] \quad (5)$$

In addition to the individual ' $\alpha$ 's referring to respective interfaces, we have calculated an effective alpha,  $\alpha_{\text{eff}}$ , for the blend with a view to compare our results with published results. The  $\alpha_{\text{eff}}$  can be written using the simple additivity rule as,

$$\alpha_{\text{eff}} = (\phi_1 + \phi_2)\alpha_{12} + (\phi_2 + \phi_3)\alpha_{23} + (\phi_3 + \phi_1)\alpha_{31} \quad (6)$$



**Figure 1:** Plot of hydrodynamic interaction parameters  $\alpha$  as a function of blend composition for the blend SAN/EVA/PVC.



**Figure 2:** Plot of hydrodynamic interaction parameters  $\alpha$  as a function of blend composition for the blend PCL/SAN/PVC.

For the ternary blend SAN/EVA/PVC, the  $\alpha_{12}$ ,  $\alpha_{23}$ ,  $\alpha_{31}$  denote the hydrodynamic interaction parameters corresponding to respective interfaces between SAN/EVA, EVA/PVC and PVC/SAN evaluated according to equation 1 and shown in figure 1. As seen from figure 1, the interface between SAN/EVA exhibits positive values for the compositions 50/15/35, 70/15/15 and 70/21/9 which suggest a weak interface. An observed small negative value for 50/35/15 suggests little compatibility between the components SAN and EVA. The interface ( $\alpha_{23}$ ) between EVA/PVC indicates negative values which are a signature of a good interface due to excess friction attributable to the physical cross-linking between EVA and PVC phases [2]. The interface ( $\alpha_{31}$ ) formed between PVC/SAN acquires negative values at all the four compositions investigated suggesting that at these compositions, good interfaces are formed. The compatibility between SAN and PVC is due to the repulsive force among the SAN chains which provide sliding pathways for PVC chains. [10]. The influence of these individual interfaces can be seen in the effective  $\alpha$  for the blend evaluated using equation 6 and also plotted in figure 1. The  $\alpha_{\text{eff}}$  is negative for the compositions 50/15/35 (measured  $T_g$ :66°C) and 50/35/15 (measured  $T_g$ :45°C) suggesting the blend is miscible at these compositions [2,11] and positive at 70/15/15 (measured  $T_g$ :44°C and 80°C) and at 70/21/9 (measured  $T_g$ :24°C and 60°C) indicating that the blend remains phase separated at these compositions [2,11].

The second blend PCL/SAN/PVC can be understood on the same lines as the SAN/EVA/PVC blend. The interfaces between PCL/SAN, SAN/PVC and PVC/PCL are characterized by  $\alpha_{12}$ ,  $\alpha_{23}$ ,  $\alpha_{31}$  respectively. The calculations have been done exactly the same way and the results are plotted in figure 2. As observed, the interface  $\alpha_{12}$  between PCL/SAN takes on both positive and negative values suggesting for the compositions for which  $\alpha$  is negative that corresponding chains are pulled closer and gives rise to the interfacial friction. Interestingly, the negative values of  $\alpha$  are observed wherever PCL is the matrix and SAN is the dispersed phase suggesting compatibility between the components. This may be due to the interaction between the carbonyl group of PCL and tertiary hydrogen of SAN, a fact well reported in literature [12].

The second interface is characterized by  $\alpha_{23}$  and this takes on a positive value at 34/33/33 composition while the other compositions result in negative values. The negative values of  $\alpha$ 's can be attributed to the repulsive force among the SAN chains paving way for PVC chains to slide in [10]. Interestingly the third interface in the blend that is between PVC/PCL, produces negative values at all the compositions studied indicating the formation of good interfaces attributable to the interaction between polar oxygen of PCL and proton of PVC [13].

Finally, the  $\alpha_{\text{eff}}$ , plotted in figure 2, shows positive values at 20/40/40 (measured  $T_g$ : -30°C and 10°C) and 34/33/33 (measured  $T_g$ : -5°C and 30°C) compositions and thus we infer the blend is immiscible at these compositions. Also the negative values at 68/16/16 (measured  $T_g$ : -15°C) and 70/25/5 (measured  $T_g$ : 10°C) indicate the blend is miscible at these compositions, in good agreement with the published literature [14].

#### 4. Conclusion:

The hydrodynamic interaction parameter ( $\alpha$ ) derived from the measured fractional free volume  $F_V$  from positron annihilation lifetime measurements, provides a simple and easy means of characterizing the individual interfaces in ternary blends. Importantly, the composition dependent miscibility level was estimated from this method. Since the information on weak interfaces is readily available, it becomes easy for the designer to choose a proper compatibilization route to stabilize that particular weak interface and so improve the overall properties of the ternary blend. Additionally,  $\alpha_{\text{eff}}$  from the present method serves as an useful parameter to infer that a given ternary blend is miscible or immiscible.

#### References:

- [1] Stamm M 2008 *Polymer Surfaces and Interfaces – Characterization, Modification and Applications* (Verlag Berlin Heidelberg: Springer)
- [2] Lizymol P P, Sabu Thomas and Jayabalan 1997 *Eur. Polym. J.* **33** 1397
- [3] Schnell M and Wolf B A 2000 *J Rheol.* **44** 617 and in 2001 *Polymer* **42** 8599
- [4] Jamieson A M, Brian G Olson and Sergei Nazarenko 2010 *Polymer Physics: From Suspensions to Nanocomposites and Beyond* ed. Utracki L A and Jamieson A M, p 491 (Hoboken: John Wiley)
- [5] Williams M L, Landel R F and Ferry J D 1955 *J. Am. Chem. Soc.* **77** 3701
- [6] Ranganathaiah C and Kumaraswamy G N 2009 *J Appl Polym Sci.* **111** 577 and references there in
- [7] Raj J M and Ranganathaiah C 2009 *J Polym Sci Part B: Polym Phys.* **47** 619
- [8] Zimm B 1956 *J Chem Phys.* **24** 269
- [9] Rouse P J 1953 *J Chem Phys.* **21** 1272
- [10] Kim J H, Barlow J W and Paul D R 1989 *Polym Eng Sci.* **29** 581
- [11] Lizymol P P and Sabu Thomas 1994 *Thermochimica Acta.* **233** 283
- [12] Chiu S C and Smith T G 1984 *J Appl. Polym. Sci.* **29** 1797
- [13] Brigitte Albert, Robert Jerome and Philippe Teyssie 1984 *Macromolecules* **17** 2552
- [14] Chiarnng Huarng J Y H, Kyonsuku Min and James L White 1988 *Polym. Eng. Sci.* **28** 1590